

■ Organic & Supramolecular Chemistry

In Situ Generation of Copper Nanoparticles by Rongalite and Their Use as Catalyst for Click Chemistry in Water

Soumya Poshala, Sanjeeva Thunga, Saikumar Manchala, and Hari Prasad Kokatla^{*[a]}

A novel, efficient and green protocol for the copper-catalyzed azide–alkyne cycloaddition (CuAAC) reaction by using copper nanoparticles (CuNPs), generated *in situ* by a green reducing agent, rongalite, is reported. Terminal alkynes reacted with benzyl, aryl and alkyl azides in the presence of copper nanoparticles and β -cyclodextrin (β -CD) in water. The reactions exclusively generated the corresponding regiospecific 1,4-

disubstituted 1,2,3-triazoles in good to excellent yields. Notably, *in situ* generation of copper nanoparticles does not require any additional stabilizing agents or special reaction conditions. β -cyclodextrin plays dual role as a stabilizing agent as well as phase transfer catalyst. This protocol is also applicable for gram scale reactions.

Introduction

Click chemistry, a Copper(I)-catalyzed azide alkyne cycloaddition (CuAAC) is a powerful tool for the synthesis of triazole-containing five-membered nitrogen heterocyclic architectures, which have broad applications in diverse areas such as medicine,^[1–4] materials,^[5–8] biological science^[4,6] and organic synthesis. Introduction of Copper(I)-catalyzed 1,3-dipolar cycloaddition of azide and alkynes by Meldal^[9] and Sharpless^[10] independently in 2002 have significantly overcome the limitations associated with Huisgen cycloadditions such as higher temperatures, low regioselectivity, resulting in mixture of 1,4 and 1,5-disubstituted 1,2,3-triazoles.

Although, a plethora of methods are known to access the 1,2,3-triazole derivatives,^[11–15] Cu(I)-catalyzed azide–alkyne cycloaddition (CuAAC) reaction remains the most efficient way to assemble the 1,2,3-triazole ring because of its 100% atom economy, exquisite selectivity, wide substrate scope, mild reaction conditions and simple purification of products.

Many reports revealed that the 1,3-dipolar cycloaddition is catalyzed by copper(I) acetylide species. But because of the instability of simple copper(I) salts, the active species are often generated *in situ* by the reduction of Cu(II) salts,^[10] oxidation of Cu(0) metal,^[16] or Cu(II)/Cu(0) comproportionation,^[17,18] Cu(I) salts directly,^[9] Cu(II) salts,^[19,20] Cu(I) complexes,^[21,22] copper containing nanoparticles,^[23,24] N-heterocyclic carbene copper complexes,^[25] Cu₂S/hu^[26] and copper nanoclusters.^[23] In some recent reports, copper species have been immobilized onto various supports such as activated charcoal,^[27] amine-functionalized polymers,^[28] and zeolites^[29] to improve recovery and reusability of catalyst.

Recently, copper nanoparticles (CuNPs) catalyzed Click chemistry has increased exponentially since the discovery of copper metal (stoichiometric ratio of turnings or powder) can be a source of the catalytic species hoping to implement green chemistry principles of reusability, efficiency and operational simplicity compared to their traditional methods. Thereafter, several methods were reported for the generation of CuNPs from bulk copper metal and copper salts. Majority of the methods involved reduction of copper salts by using suitable reducing agents, i.e., NaBH₄, Li, N₂H₄·H₂O etc.^[30–32] However, copper nanoparticles are unstable as and vigorously react with atmospheric oxygen to readily form Cu₂O then CuO. Therefore, stabilizing agents such as oleic acid, PVP, CTAB, sodium metaphosphate, ascorbic acid, ethylene glycol, fructose etc. are essential for their stabilization. Nature of the nanoparticles depends on many factors including solvents, temperature, time, concentration of solution and reducing agents. Consequently, broad spectrum of both homogeneous^[33,34] and heterogeneous catalytic^[35–37] systems has emerged. Recently, Alonso *et al.* demonstrated that CuNPs accelerate the one-pot click reaction involving the ring opening of an epoxide with azides followed by its cycloaddition with alkyne.^[38–42]

In literature we found that most of the reports of CuAAC are used CuNPs directly from commercial sources or synthesized separately prior to their use in the reactions. The latter one involved the use of copper salts and reducing agents, most of which are hazardous to the environment. Therefore, there is a search for environmentally benign cost effective and operationally simple method for such cycloaddition reactions. Herein, we report a green method for the *in situ* generation of CuNPs by using a cheaper, green reducing agent, sodium hydroxymethanesulfinate (Rongalite). Rongalite is readily available reagent and exhibits several industrial applications. It is used as a (i) decolorizing agent in the textile and sugar industries (ii) bleaching agent in the printing and dyeing industry^[43] (iii) antidote for heavy metal poisoning (iv) reducing agent in polymerization (v) bactericide and fungicide in veterinary industry (vi) photographic developer (vii) reagent in the

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synthesis of sultines, sulfones, spirooxindoles, sulfides, thioesters, selenoesters and allyl alcohols etc., (viii) source of C1 unit in the synthesis of 2,4,5-trisubstituted furans.^[43–49] Furthermore, this approach avoids some of the steps required for the prior preparation of CuNPs such as centrifugation, washing and drying of nanoparticles and their further stabilization.

Results and Discussion

In this report, we have examined the feasibility to synthesize the copper nanoparticles from copper(II) salts *in situ* by green reducing agent rongalite, the potential catalyst for click ligation. For our initial screening experiments, the CuAAC reaction between benzyl azide, and phenyl acetylene was chosen as the model reaction (Table 1).

Entry	Solvent	CuSO ₄ ·5H ₂ O (equiv.)	Rongalite (equiv.)	β -CD (equiv.)	Time	Yield (%) ^[b]
1	THF/H ₂ O	0.1	0.1	-	5 h	60
2	THF/H ₂ O	0.1	0.2	-	3 h	68
3	THF/H ₂ O	0.1	0.3	-	2 h	70
4	THF/H ₂ O	0.1	0.5	-	1 h	70
5	DMF/H ₂ O	0.1	0.5	-	50 min	60
6	DMSO/H ₂ O	0.1	0.5	-	40 min	65
7	Dioxane/H ₂ O	0.1	0.5	-	40 min	80
8	EtOH/H ₂ O	0.1	0.5	-	1 h	50
9	CH ₃ CN/H ₂ O	0.1	0.5	-	12 h	15
10	<i>t</i> -BuOH/H ₂ O	0.1	0.5	-	1 h	70
11	H ₂ O	0.1	0.5	0.01 ^[c]	40 min	92
12	H ₂ O	0.1	0.5	0.02	10 min	95
13	H ₂ O	0.05	0.5	0.02	20 min	60

[a] Reactions were carried out by using **1a** (1.0 mmol), **2a** (1.1 mmol) and CuSO₄·5H₂O (0.1 mmol) in 2.0 mL solvent (1:1), unless otherwise mentioned. [b] Yield where reported is of isolated and purified product. [c] Reaction was conducted in presence of β -Cyclodextrin.

We observed that when the reaction of the benzyl azide **1a** (1.0 mmol) with phenyl acetylene **2a** (1.1 mmol) catalyzed by *in situ* generated CuNPs from CuSO₄·5H₂O (0.1 equiv.) and rongalite (0.1 equiv.), in mixture of THF/ H₂O (1:1) (2 mL), for 5 h, the corresponding 1,4-disubstituted 1,2,3-triazole **3a** was obtained in 60% yield (Table 1, entry 1). These results prompted us to optimize the reaction conditions to improve the product yield. We examined the effect of the reducing agent on reaction yield by increasing the loading of reducing agent to 0.2 equiv., 0.3 equiv. and 0.5 equiv. (Table 1, entries 2–4), surprisingly 0.5 equiv. of rongalite gave improved yield in less time (Table 1, entry 4). Next, we have carried out the reaction

in various solvents to assess their effect on the reaction efficiency. For this we performed the reactions in mixture of solvents DMF/H₂O, DMSO/H₂O, dioxane/H₂O, EtOH/H₂O, CH₃CN/H₂O, *t*-BuOH/H₂O (Table 1, entries 5–10). These results proved that dioxane/H₂O solvent system is best for our reaction to furnish triazoles in good yield in less time (Table 1, entry 7).

Since the green chemistry principles are emerging to maximize the use of environmentally benign protocols toward the ecological and economic advantages, performing CuAAC in aqueous media is becoming popular, but remains challenging for chemists.^[38,42,50–52] During the course of further optimization of the reaction conditions, we noticed that addition of β -cyclodextrin as a phase transfer catalyst improved the yield and time with 95% and 10 min respectively (Table 1, entry 12). These results were consistent with those reported by Lim et al.^[53] However, lowering the CuNPs loading, decreases the product yield (Table 1, entry 13).

Further, we examined other sulphur-containing reducing agents for *in situ* generation of CuNPs from Cu(II) salts and click ligation, results are shown in Table 2.

Entry	Copper salt	Reducing agent	Time	Yield (%) ^[b]
1	CuSO ₄ ·5H ₂ O	Rongalite	10 min	95
2	CuSO ₄ ·5H ₂ O	Sodium dithionite	24 h	50
3	CuSO ₄ ·5H ₂ O	Thiourea dioxide	2 h	80
4	CuCl ₂	Rongalite	20 min	60
5	CuCl ₂	Sodium dithionite	24 h	30
6	CuCl ₂	Thiourea dioxide	18 h	45
7	Cu(OAc) ₂ ·H ₂ O	Rongalite	20 min	70
8	Cu(OAc) ₂ ·H ₂ O	Sodium dithionite	24 h	40
9	Cu(OAc) ₂ ·H ₂ O	Thiourea dioxide	1.5 h	87

[a] Reactions were carried out by using **1a** (1.0 mmol), **2a** (1.1 mmol) and CuSO₄·5H₂O (0.1 mmol) and β -cyclodextrin (0.02 mmol) in H₂O (2.0 mL), unless otherwise mentioned. [b] Yield where reported is of isolated and purified product.

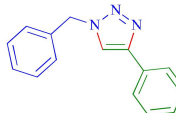
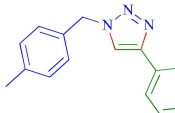
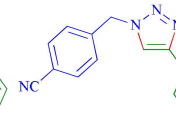
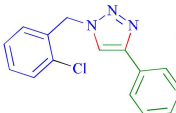
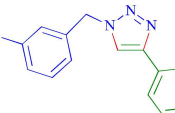
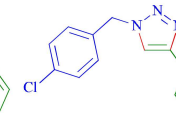
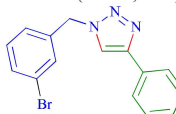
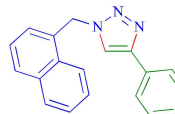
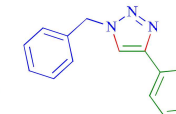
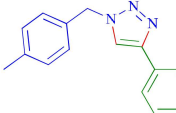
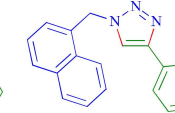
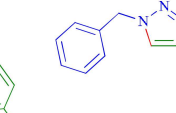
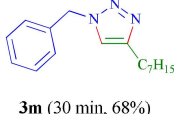
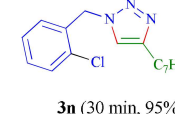

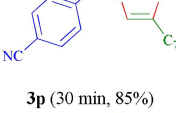
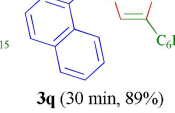
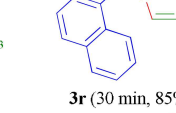

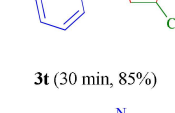
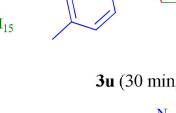
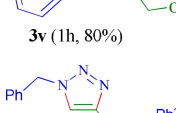
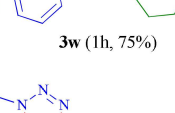
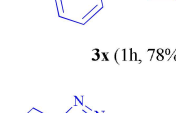
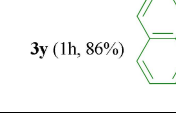
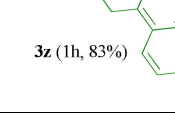
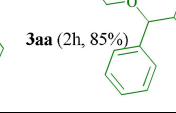
Our data indicates that rongalite is the best reducing agent among the other sulphur-containing reducing agents (Table 2, entry 1). Although, thiourea dioxide and sodium dithionite are capable of generating CuNPs, but they produce the 1,2,3-triazoles in less yield with longer time.

With optimized reaction conditions (Table 1, entry 12), we have applied same condition to various benzyl azides with substituted alkynes (Table 3).

Firstly, various benzyl azides were treated with phenyl acetylene and alkyl acetylenes (Table 3). Benzyl azide reacted smoothly with phenyl acetylene to give 1,2,3-triazole **3a** in excellent yield (Table 3).

We have further investigated the effect of substituents on benzyl azide and found that a little effect on the product yields (Table 3, **3b–c**). *Para*-substitution of Me and CN groups did not

Table 3. Click reaction of benzyl azides with various alkynes using β -Cyclodextrin (β -CD) and rongalite in water.^[a,b]

R_1-N_3 1a-h	$\equiv R_2$ 2a-j	$\xrightarrow[\text{Rongalite, } \beta\text{-CD}]{\text{CuSO}_4 \cdot 5\text{H}_2\text{O}}$ $\text{H}_2\text{O, rt}$	$R_1-N-N-N-R_2$ 3a-3aa
			
3a (20 min, 95%)	3b (30 min, 94%)		3c (30 min, 95%)
			
3d (30 min, 93%)	3e (30 min, 80%)		3f (30 min, 85%)
			
3g (30 min, 92%)	3h (30 min, 99%)		3i (30 min, 91%)
			
3j (30 min, 82%)	3k (30 min, 90%)		3l (30 min, 70%)
			
3m (30 min, 68%)	3n (30 min, 95%)		3o (30 min, 99%)
			
3p (30 min, 85%)	3q (30 min, 89%)		3r (30 min, 85%)
			
3s (30 min, 92%)	3t (30 min, 85%)		3u (30 min, 89%)
			
3v (1h, 80%)	3w (1h, 75%)		3x (1h, 78%)
			
3y (1h, 86%)	3z (1h, 83%)		3aa (2h, 85%)

[a] Reactions were carried out by using azides **1a-h** (1.0 mmol), alkynes **2a-j** (1.1 mmol), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.1 mmol) and β -cyclodextrin (0.02 mmol) in H_2O (2 mL). [b] Yield where reported is of isolated and purified product.

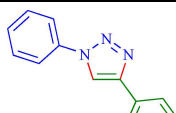
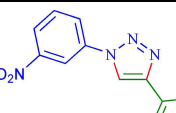
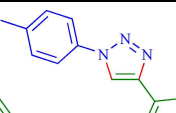
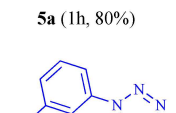
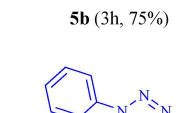
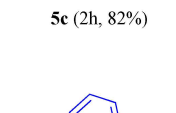
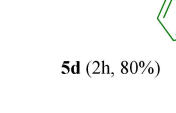
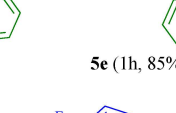
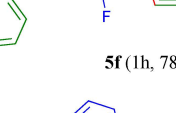
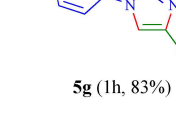
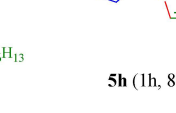
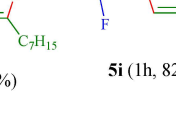
affect the reaction outcome in terms of product yield. Halogen (at *ortho* as well as *para* positions) substituted benzyl azides

also reacted smoothly to give the corresponding 1,2,3-triazoles in good yields (Table 3, **3d-g**). 1-(Azidomethyl)naphthalene gave cycloadduct quantitatively with phenyl acetylene (Table 3, **3h**). Notably, 4-tert-butyl-phenylacetylene gave less yield compared to phenyl acetylene (Table 3, **3i-k**).

Aliphatic long chain alkynes and alkynes containing polar groups also participated in our protocol for CuAAC reaction without any hurdle (Table 3, **3l-x**). It is worth noting that increasing aromatic rings on alkynes did not alter the yields of the products (Table 3, **3y-3aa**).

Later, we applied our green protocol to aromatic azides and phenyl acetylenes and results are shown in (Table 4).

Table 4. Click reaction of aryl azides with various alkynes using β -Cyclodextrin (β -CD) and rongalite in water.^[a,b]

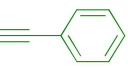

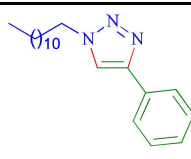
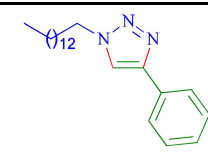
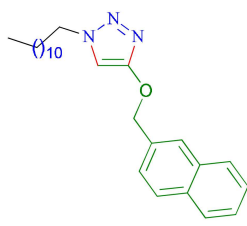
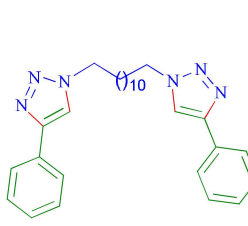
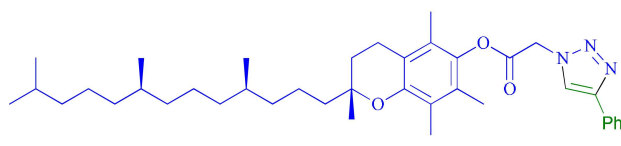
$\text{Ar}-N_3$ 4a-f	$\equiv R_2$ 2a, c-g	$\xrightarrow[\text{Rongalite, } \beta\text{-CD}]{\text{CuSO}_4 \cdot 5\text{H}_2\text{O}}$ $\text{H}_2\text{O, rt}$	$\text{Ar}-N-N-N-R_2$ 5a-k
			
5a (1h, 80%)	5b (3h, 75%)		5c (2h, 82%)
			
5d (2h, 80%)	5e (1h, 85%)		5f (1h, 78%)
			
5g (1h, 83%)	5h (1h, 80%)		5i (1h, 82%)
			
5j (1h, 85%)	5k (1h, 86%)		

[a] Reactions were carried out by using azides **4a-f** (1.0 mmol), alkynes **2a, c-g** (1.1 mmol) and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.1 mmol) and β -cyclodextrin (0.02 mmol) in H_2O (2 mL). [b] Yield where reported is of isolated and purified product.

Unsubstituted phenyl azide and electron donating group containing phenyl azides gave corresponding triazoles in comparable yields, whereas electron withdrawing aromatic azides gave less yield in more time compare to phenyl azide (Table 4, **5a-c**). Further, halogen containing phenyl azides also participated smoothly in cycloaddition reaction and gave 1,4-disubstituted-1,2,3-triazoles in good yields (Table 4, **5d-e**). Also

reactivity of aliphatic alkynes was comparable to the aromatic alkynes (Table 4, 5f-k).

It is noteworthy that aliphatic long chain azides also participated in CuAAC reaction to give of triazole in good yield (Table 5, 7a-b). We have observed the downfall in reaction

Table 5. Click reaction of aliphatic azides with various alkynes using β -Cyclodextrin (β -CD) and rongalite in water. ^[a,b]		
R_1-N_3 6a-d	+ 	$\xrightarrow[\text{Rongalite, } \beta\text{-CD, H}_2\text{O, rt}]{\text{CuSO}_4 \cdot 5\text{H}_2\text{O}}$ 
 7a (30 min, 70%)	 7b (30 min, 61%)	
 7c (1h, 73%)	 7d (2h, 70%)	
 7e (4h, 60%)		
<p>[a] Reactions were carried out by using azides 6a-d (1.0 mmol), alkynes 2a, h (1.1 mmol) and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.1 mmol) and β-cyclodextrin (0.02 mmol) in H_2O (2 mL). [b] Yield where reported is of isolated and purified product.</p>		

yields when chain length of aliphatic azides is increased, due to the solubility problem. To our delight, 1,12-diazido-dodecane also easily underwent click reaction with benzyl azide in 2 h to yield 70% of bis-triazole product (Table 5, 7d). Bulky molecules like tocopherol is also tolerable with this new method (Table 5, 7e).

Although, there are several reports on CuAAC reactions catalyzed by CuNPs and most of them require high temperature (60–80 °C) and longer time (2–24 h),^[38,41–42] reactions using our method require ambient temperature and shorter reaction time (30 min–2 h) to furnish the triazoles in water.

Further, we investigated the reaction mechanism of CuAAC catalyzed by CuNPs. Also we found in the literature that rongalite is capable of converting copper(II) chloride into nanoparticles such as Cu and Cu_2O at higher temperature (70–100 °C).^[54–56] These findings arose our interest to analyze the composition of copper complex to know the type of copper

species present and responsible for click reaction. For this, CuNPs were prepared according to the following protocol: To a 20 mL of 0.5 molar $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution in a beaker were added β -cyclodextrin (0.02 equiv.) and rongalite (5 equiv.) and stirred at room temperature for 10 minutes. Finally, we observed the formation of blackish brown colour precipitate from blue colour (Figure 1, a–e), which was then centrifuged at

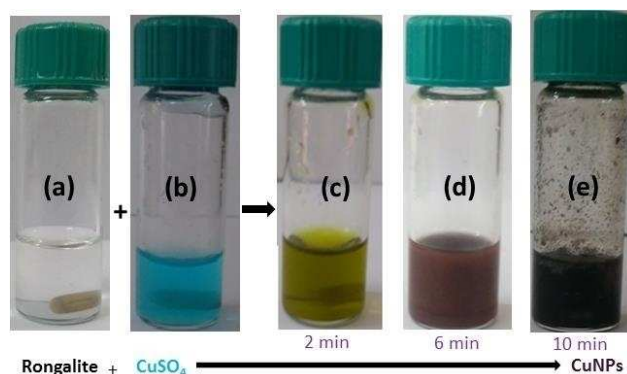


Figure 1. Color change observed during the copper nanoparticles formation.

10000 rpm for 15 min, washed with water (5 times) and dried under inert condition. The dried powder was analyzed by powder XRD (PXRD).

The powder XRD studies were carried out in order to investigate both the crystal structure and the average crystallite size of nanoparticles (Figure 2). The PXRD patterns is indexed

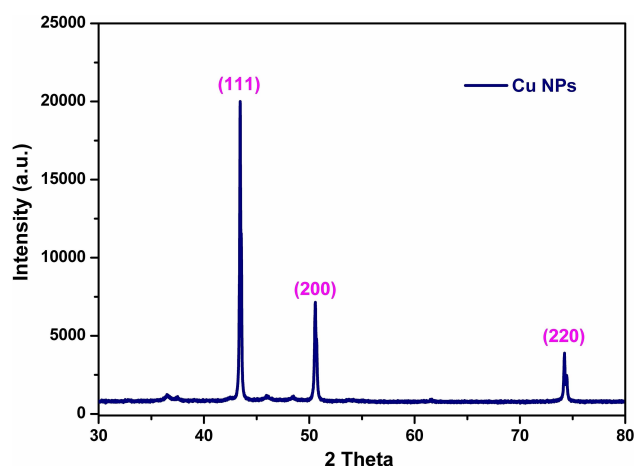


Figure 2. Powder XRD pattern of synthesized Cu-NPs.

the presence of face centered cubic (f.c.c.) Cu (JCPDS, card no. 04–0836). The peaks at 43.36°, 50.48°, 74.35° belong to (111), (200), (220) planes of Cu nanoparticles. The average crystallite size was determined by using Scherrer's equation.

Crystallite size = $k\lambda/\beta\cos\theta$. Where k is dimensionless shape factor = 0.9, λ is X-ray wavelength = 1.54 Å, β is full width of

half maxima in radians, θ is angle of diffraction. The calculated average crystallite size of CuNPs is about to be 39 nm.

Powder XRD data suggested that the sample contains only Copper(0) NPs (Figure 2). Flores-López et al.,^[57] proved that cyclodextrins are good stabilizing agents in the formation of Cu nanoparticles and our results are consistent with reported method.

SEM was carried out to know the morphological characteristics of formed Cu nanoparticles (Figure 3). Image of Figure 3

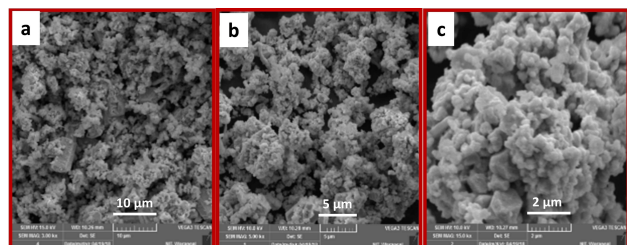


Figure 3. SEM images of Cu-NPs in different magnifications a) 10 μm ; b) 5 μm ; c) 2 μm

(a, b, c) is the group of SEM images which clearly shows the formation of 'Cu' nanoparticles with irregular shape and the formed nanoparticles are agglomerated.

The plausible reaction mechanism pathway proposed for the reaction is the same as in earlier reports.^[10,16] The Cu(0)NPs were generated *in situ* by rongalite from copper salt via single electron transfer.^[56] Then the Cu(0)NPs reacts with an alkyne to give a copper-acetylide. The 1,3-dipolar cyclization of the resulting Cu acetylide and an organic azide followed by the protonation provided the formation of a triazole and the regeneration of Cu(0) catalyst (Scheme 1).^[58,59]

Conclusions

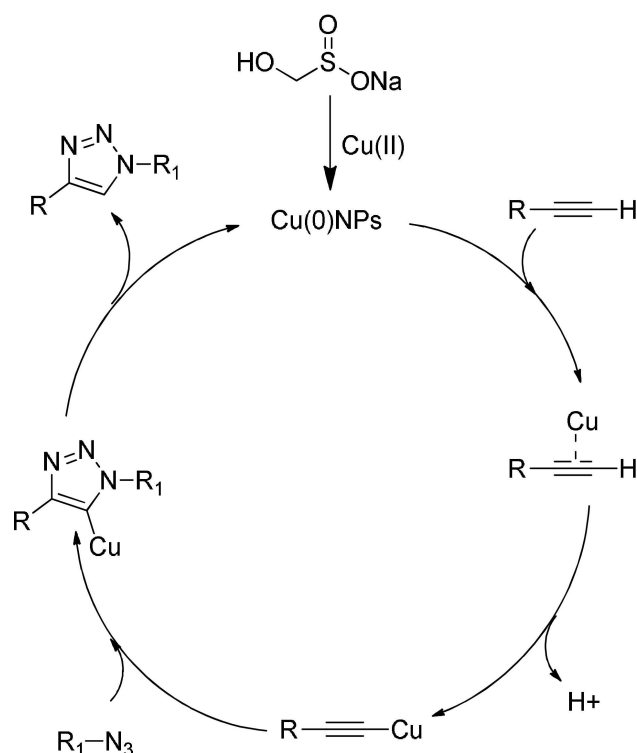
In summary, a green protocol using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ /Rongalite catalyst system, which generates CuNPs *in situ* provides the regiospecific 1,4-disubstituted 1,2,3-triazoles in excellent yields with relatively short reaction times. Additionally, this protocol allows to a wide range of functional groups on both the alkyne and azide part. Here, β -cyclodextrin is playing dual role of both stabilizing agent as well as phase transfer catalyst. This method is also applicable for gram scale synthesis.

Supporting Information Summary

Detailed experimental procedure, characterization data (^1H , ^{13}C NMR spectra) for all synthesized products **3 a-3 aa**, **5 a-k** and **7 a-e** are available in the Supporting Information.

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Scheme 1. Proposed mechanism for the CuAAC reaction.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Click Reaction • CuNPs • In situ • Rongalite • Triazoles

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